# Organic and Biological Chemistry

## Chemical Reactions under High Pressure. XIII. The Activation Volumes of Some Solvolysis Reactions[1]

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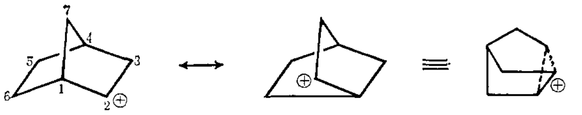
**Abstract:** The activation volumes of *exo*- and *endo*-2-norbornyl brosylate have been measured; the former is less negative by several cubic centimeters/mole. This is interpreted in terms of the Drude–Nernst equation for electrostriction. The observation is consistent with the assumption that the transition state of the *exo*-brosylate is characterized by charge delocalization. The same conclusion applies to *endo*-3-*cis*-bicyclo[3.1.0]hexyl tosylate when this is compared to its *exo* isomer. The activation volumes of several monocyclic tosylates ($C_4$–$C_8$) were also measured; the pressure acceleration for $C_4$ is somewhat smaller than that for the others. The pressure effect on the solvolysis rate of *anti*-7-norbornenyl tosylate is larger than that of any of the other substrates; it is suggested that this is an indication of $\pi$-electron participation. This is further supported by the fact that among several benzenesulfonate esters differing only in their ability to form symmetrical transition states through $\pi$ participation, those substrates able to do so have the more negative activation volumes.

It was shown in a recent communication[2] that the solvolysis of *exo*-2-norbornyl brosylate is characterized by a smaller activation volume than those of its *endo* epimer and of cyclopentyl brosylate. An argument was made that this is consistent with the controversial idea that participation by a neighboring $\sigma$ bond is occurring in the transition state of the *exo*-brosylate. This participation would presumably disperse the incipient positive charge between the $C_1$ and $C_2$ carbon atoms.



The diffuse charge is thought to be less effective than a localized charge in attracting the surrounding solvent, and hence volume diminution is less pronounced than it would otherwise be. Since the effect is small and may conceivably be masked by such unknown, coincidental factors as the packing efficiency of solvent molecules around the substrates, it was clearly desirable to look for further examples. We report here in addition the effect of hydrostatic pressure on the solvolysis rates of *exo*- and *endo*-3-*cis*-bicyclo[3.1.0]hexyl tosylates, of a number of cycloalkyl tosylates ($C_4$–$C_8$), of *anti*-7-norbornenyl tosylate, and of several pairs of saturated and unsaturated nitrosylates, and further discuss the premise of this method.

### Experimental Section

**Materials.** Acetone was treated with potassium permanganate and Drierite at room temperature for 2 days and fractionated through a 50-cm Fenske column filled with glass helices.[3] The *exo*-2-norborneol, cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, cholesterol, and 5-$\alpha$-cholestan-3$\beta$-ol used were commercial materials. *endo*-2-Norborneol,[4] *anti*-7-norbornenol,[5] cyclobutanol,[6] 2-($\Delta^2$-cyclopentenyl)ethanol,[7] 2-($\Delta^3$-cyclopentenyl)ethanol,[8] 2-cyclopentylethanol,[7] 2-($\Delta^3$-cyclohexenyl)ethanol,[8] 2-cyclohexylethanol,[9] ($\Delta^4$-cycloheptenyl)methanol,[10] cycloheptylmethanol,[11] and *exo*- and *endo*-3-*cis*-bicyclo[3.1.0]hexanol[12] were prepared as described in the references and converted into the brosylates or tosylates as described by Winstein and Trifan[13] and Brown and Ham;[14] the nitrosylates were prepared by the method of Lee and Wong[7] and crystallized from hexane. The melting points agreed in nearly all cases with those reported; 2-($\Delta^2$-cyclopentenyl)ethyl nitrosylate in our hands had a somewhat higher melting point (68°) than the reported value (63–64°).[7] The *exo*-3-*cis*-bicyclo[3.1.0]hexyl tosylate was freed from the *endo* isomer by 12 hr of solvolysis in 60:40 acetone–water (w/w) mixtures at 40°, followed by extraction with ether and crystallization of the residue from pentane–ether mixtures. Previously unreported esters are listed with their melting points and analytical data in Table I.

**Measurements.** The apparatus described previously[15] was used without modification. Samples of about 15 ml containing about 15 mg of the ester were used for each measurement; after reaction, these solutions were quenched with cold acetone and titrated with 0.01 *N* sodium hydroxide and the mixed indicator described by Kiefer and Roberts.[16] The reactions were followed to 40–60% of completion; four to six measurements were used in each case to evaluate the rate constants, which are estimated to be reliable to 2–3%. The observed rates are summarized in Table II. Although differences in solvent, temperature, and leaving group preclude direct comparisons of our results at atmospheric pressure with literature data, they are in all cases substantially in agreement. The activation volumes were obtained by machine computation from

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] W. J. le Noble and B. L. Yates, *J. Am. Chem. Soc.*, **87**, 3515 (1965).

[3] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

[4] C. F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

[5] P. R. Story, *ibid.*, **26**, 287 (1961).

[6] R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Am. Chem. Soc.*, **83**, 4843 (1961).

[7] C. C. Lee and E. W. C. Wong, *Tetrahedron*, **21**, 539 (1965).

[8] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

[9] S. Ishiwata and T. Nozaki, *J. Pharm. Soc. Japan*, **71**, 1261 (1951); *cf. Chem. Abstr.*, **46**, 5590*a* (1952).

[10] (a) G. Le Ny, *Compt. Rend.*, **251**, 1526 (1960); (b) H. Felkin, G. Le Ny, L. Lion, W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Letters*, 157 (1966).

[11] E. E. Royals and A. H. Neal, *J. Org. Chem.*, **21**, 1448 (1956).

[12] S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235, 3244 (1961).

[13] S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

[14] H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

[15] W. le Noble, *ibid.*, **85**, 1470 (1963).

[16] E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962).

**Table I.** Melting Points and Analytical Data for the *p*-Nitrobenzenesulfonate Esters

| Ester[a] | Mp, °C | % C | | % H | | % N | | % S | |
|---|---|---|---|---|---|---|---|---|---|
| | | Theor | Found | Theor | Found | Theor | Found | Theor | Found |
| XV | 64.5–65 | 54.00 | 53.86 | 5.50 | 5.67 | 4.50 | 4.70 | 10.30 | 10.55 |
| XVI | 73.5–74 | 53.66 | 53.89 | 6.11 | 6.17 | 4.47 | 4.64 | 10.23 | 10.51 |
| XVII | 85–85.5 | 54.00 | 54.21 | 5.50 | 5.55 | 4.50 | 4.50 | 10.30 | 10.53 |
| XVIII | 88.5–89 | 53.66 | 53.71 | 6.11 | 6.42 | 4.47 | 4.52 | 10.23 | 10.50 |
| XIX | 118 dec | 69.31 | 69.22 | 8.64 | 8.61 | 2.45 | 2.82 | 5.61 | 5.92 |
| XX | 119 dec | 69.07 | 69.08 | 8.96 | 9.00 | 2.44 | 2.41 | 5.59 | 5.89 |

[a] See Table IV below for the structures corresponding to these numerals.

**Table II.** Rate Constants, $10^6 k_1$ ($\text{sec}^{-1}$), at Various Pressures[a]

| Substr[b] | *P*, kbar 0.00 | 1.03 | 2.07 | 3.10 | 4.13 |
|---|---|---|---|---|---|
| I | 40.8 | 71.8 | 103 | 144 | 182 |
| II | 0.229 | 0.464 | 0.705 | 0.945 | 1.23 |
| III | 7.12 | 14.6 | 23.3 | 33.8 | 47.9 |
| IV | 43.6 | 79.4 | 121 | 172 | 220 |
| V | 41.9 | 82.7 | 134 | 202 | 298 |
| VI | 1.55 | 3.08 | 5.07 | 7.71 | 11.3 |
| VII | 50.4 | 101 | 164 | 247 | 352 |
| VIII | 4.02 | 7.97 | 12.8 | 18.4 | 26.0 |
| IX | 49.3 | 84.5 | 126 | 184 | 245 |
| X | 2.53 | 5.06 | 8.17 | 12.2 | 18.0 |
| XI | 4.34 | 9.39 | 15.9 | 23.5 | 31.9 |
| XII | 29.6 | 66.6 | 102.6 | 141 | 197 |
| XIII | 7.52 | 15.1 | 23.0 | 33.7 | 44.6 |
| XIV | 8.92 | 14.2 | 22.0 | 31.9 | 45.6 |
| XV | 11.11 | 20.6 | 33.3 | 51.4 | 73.6 |
| XVI | 10.2 | 18.9 | 29.8 | 44.4 | 66.1 |
| XVII | 48.4 | 107.5 | 147 | 197 | 265 |
| XVIII | 2.42 | 4.15 | ... | 8.81 | 12.0 |
| XIX | 4.68 | ... | ... | ... | ... |
| XX | 1.33 | ... | ... | ... | ... |

[a] See Tables III and IV for the temperatures and solvent compositions. [b] See Tables III and IV for the structures corresponding to these numerals.

the expressions $\Delta V^* = -RT\delta \ln k/\delta p$ and $\ln k = ap^2 + bp + c$. They are accurate to (0.5–1) cm³/mole; no reliable data for the steroidal esters could be obtained because of the low solubilities of these esters.

## Results and Discussion

It is now a well-established fact that the ionization of a neutral molecule is characterized by a decrease in volume, in spite of the fact that the two particles, at a distance equal to the bond length in the neutral molecule, recede from one another to at least the sum of their ionic radii in the process. This phenomenon can be readily demonstrated and its magnitude determined by comparing the densities of solutions of, *e.g.*, acetic acid, sodium acetate, sodium chloride, and hydrochloric acid. Such data enable one to calculate the partial molal volumes of these species, and hence the volume change for the process

$$\text{AcOH}_{(\text{aq})} \longrightarrow \text{H}^+{}_{(\text{aq})} + \text{OAc}^-{}_{(\text{aq})}$$

as $\Delta\bar{V} = \bar{V}_{\text{HCl}} + \bar{V}_{\text{NaOAc}} - \bar{V}_{\text{NaCl}} - \bar{V}_{\text{AcOH}}$. Its magnitude can also be determined from the change in $K_a$ with hydrostatic pressure, by the use of the relation

$$\Delta\bar{V} = -RT\delta \ln K/\delta p$$

This volume change is invariably negative for both acids and bases. On the average, its magnitude for monobasic acids in water is about −15 cm³/mole; it is undoubtedly the result of the very large forces that ions exert on surrounding solvent molecules and a reflection of the resulting compression (electrostriction).

This effect can be demonstrated not only with acid and base equilibria but also with reactions characterized by a highly polar transition state. The volume decrease that has occurred when the transition state has been reached can, of course, not be determined from density measurements, but must be calculated from the pressure coefficient of the rate constant by means of the expression

$$\Delta V^* = -RT\delta \ln k/\delta p$$

Many of such activation volumes have been measured, and in those instances where ionization is one of the features of the reaction (solvolysis, the Menshutkin reaction, nucleophilic aromatic substitution, etc.), $\Delta V^*$ is invariably negative. Its magnitude in water is comparable to the electrostriction term for electrolytes described above. Conversely, equilibrium and rate constants of reactions characterized by neutralization of charge are invariably decreased by the application of pressure.[17]

An early attempt was made by Drude and Nernst[18] to derive an expression for this phenomenon, which led to

$$\Delta V_i = -(q^2/2rD^2)(D/p)$$

where $\Delta V_i$ is the volume change that accompanies the transfer of an ion of charge $q$ and radius $r$ from a vacuum to a fluid of dielectric constant $D$. The derivation is based on the assumption of a continuous medium: $\Delta V_i$ is considered to be independent of the sign of the charge. There is much support for this assumption, as there is for the predicted dependence on the size of the ion and for that on the medium;[17] however, in the present paper we will restrict our attention to the correlation of $\Delta V_i$ and $\Delta V^*$ with the magnitude of the charge.

If we assume for the moment that the charge dependence is indeed correctly shown by the Drude–Nernst equation, an application comes to mind in the form of the carbonium ion problem and the related question of participation. The basic question here is whether in favorable circumstances a carbonium ion, or an incipient carbonium ion, can be stabilized to any degree by charge delocalization to singly bound carbon atoms.[19] Thus, if *exo*-2-norbornyl esters solvolyze with

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(17) References to this subject may be found in W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

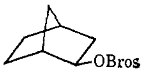
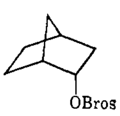
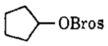
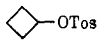
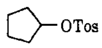
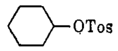
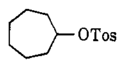
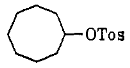
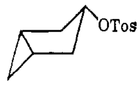
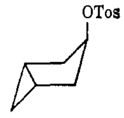
(18) P. Drude and W. Nernst, *Z. Phys. Chem.*, **15**, 79 (1894).

(19) For recent reviews, see: (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) H. C. Brown, *Chem. Brit.*, 199 (1966); (c) G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); (d) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966). For some very interesting recent additions see B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Wershiuk, *J. Am. Chem. Soc.*, **89**, 1730 (1967); J. M. Jerkumica, S. Borčić, and D. E. Sunko, *ibid.*, **89**, 1732 (1967); E. J. Corey and R. S. Glass, *ibid.*, **89**, 2600 (1967).

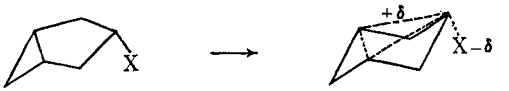
participation of the 1,6 electrons and their *endo* epimers solvolyze without such assistance,[13] the positive charge in the transition state of the former reaction would be more diffuse than in that of the latter. In the absence of unforeseen complications the volume decrease therefore should be less severe for the *exo* species during solvolysis, and the activation volume characterizing it should be less negative.

The results, partially listed in Table III, bear this prediction out. The activation volume for the *exo* epimer is about −14 cm$^3$/mole, whereas that of the *endo* species and that of cyclopentyl brosylate are both about −18 cm$^3$/mole. A similar claim has been made for the *exo*- and *endo*-3-*cis*-bicyclo[3.1.0]hexyl tosylates, the *endo* epimer now being assisted.[12]

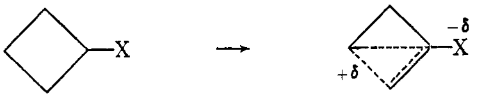
**Table III.** Activation Volumes in the Solvolysis of Several Benzenesulfonates

| Substrate | | Temp, | Solvent, wt % | $\Delta V_0^*$,[a] |
|---|---|---|---|---|
| No. | Structure | °C | acetone | cm$^3$/mole |
| I |  | 40.00 | 94.0 | −14.3 |
| II |  | 40.00 | 94.0 | −17.8 |
| III |  | 40.00 | 94.0 | −17.7 |
| IV |  | 40.00 | 70.0 | −15.8 |
| V |  | 40.00 | 70.0 | −17.0 |
| VI |  | 40.00 | 70.0 | −17.5 |
| VII |  | 40.00 | 70.0 | −17.7 |
| VIII |  | 25.00 | 70.0 | −16.5 |
| IX |  | 40.00 | 70.0 | −14.0 |
| X |  | 40.00 | 70.0 | −17.2 |

[a] The computed curves fitted the observed rate constants with a correlation constant larger than 0.99 in all cases. The correlation constants were calculated as recommended by F. E. Croxton, "Elementary Statistics with Applications in Medicine," Prentice-Hall, Inc,, New York, N. Y., 1953, pp 158–159.



In this case also this claim is consistent with the result that the *endo* ester has an activation volume of −14 cm$^3$/mole; the *exo* isomer and cyclohexyl tosylate have activation volumes of about −17 cm$^3$/mole. Finally, among a series of cycloalkyl tosylates, earlier studies by Roberts[20] had led to a suggestion that participation intervened in that case.



The activation volumes among the cycloalkyl tosylates ($C_4$–$C_8$) shown in Table III once again show the observed effect to be consistent with these views, although the effect is smaller than in the earlier examples, and is only barely outside experimental uncertainty. It should be noted that the transition state of cyclobutyl tosylate is not as symmetrical as those of the *exo*-2-norbornyl and *endo*-3-*cis*-bicyclo[3.1.0]hexyl esters; *i.e.*, not all the contributing structures are identical. Hence charge dispersal may be less pronounced.

As the work progressed, we became aware that several years earlier Hamann[21] had measured the activation volumes for the methanolysis of both ethyl bromide and allyl bromide, and found values of about −30 and −35 cm$^3$/mole, respectively. The experiments had not been run with the purpose of giving accurate relative values; for instance, a different type of apparatus was evidently used for the two experiments, and they were done at different temperatures. Nevertheless, there seems to be no doubt about the conclusion that the allylic species, the rate of which is surely enhanced by charge delocalization, is accelerated *more* by pressure than is ethyl bromide. Furthermore, we found that the activation volume of *anti*-7-norbornenyl tosylate was more negative than that of any of the substrates examined earlier, as detailed below.

In a sense the phenomenon of participation in the substrates mentioned earlier is different from that in allylic substrates in that $\sigma$ electrons are involved in the former and $\pi$ electrons in the latter. It is a well-known fact that a $\pi$ orbital is relatively voluminous; thus, in order to calculate a molar volume from atomic parachor contributions, one must add 18 cm$^3$/mole for every carbon–carbon double bond present in the molecule.[22] Hence, if a molecule is undergoing solvolysis faster because of participation by a double bond, the transition state will be characterized not only by charge delocalization, which would diminish the volume decrease, but also by the partial loss of a double bond which would enlarge it.[23]

With that thought, we studied a number of molecules in which participation by more distant double bonds is involved (see Table IV). *anti*-7-Norbornenyl tosylate[24] had already been found to have an activation volume of −20 cm$^3$/mole, more negative than any other benzenesulfonate ester we had studied under similar condi-

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(20) See, *e.g.*, M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961), and papers quoted therein.

(21) H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **50**, 1188 (1954); H. G. David, S. D. Hamann, and D. R. Teplitzky, *Discussions Faraday Soc.*, **22**, 119 (1956).

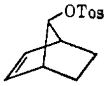
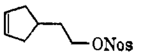
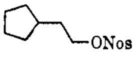
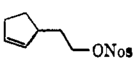
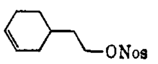
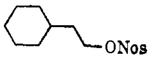
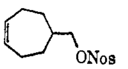
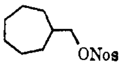
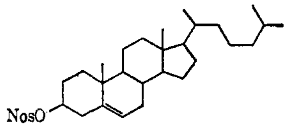
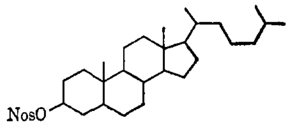
(22) O. R. Quayle, *Chem. Rev.*, **53**, 439 (1953). The referee commented: ". . . it is more sensible to ascribe the increment of volume per $\pi$ bond to the associated open connection." We agree that the increment is probably the sum of several terms, but have made no attempt here to dissect it.

(23) To our knowledge, Hamann is the only other investigator to have stated this proposition (S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press Inc., New York, N. Y., 1957, p 185); he writes that the rate acceleration in the conversion of citral to *p*-menth-1-ene-3,8-diol "probably arises from the intrinsic decrease in volume of the molecules when they form bridged complexes."

(24) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

tions. Unfortunately, this compound is so much more reactive[25] than either the *syn* epimer or 7-norbornyl tosylate that a direct comparison under the same conditions is not possible.

**Table IV.** Activation Volumes in the Solvolysis of Several Benzenesulfonates

| Substrate | | Temp, °C | Solvent, wt % acetone | $\Delta V_0^*$,[a] cm$^3$/mole |
|---|---|---|---|---|
| No. | Structure | | | |
| XI |  | 25.00 | 94.0 | −19.7 |
| XII |  | 40.00 | 65.0 | −19.1 |
| XIII |  | 40.00 | 65.0 | −17.2 |
| XIV |  | 40.00 | 65.0 | −12.3 |
| XV |  | 40.00 | 65.0 | −15.1 |
| XVI |  | 40.00 | 65.0 | −15.9 |
| XVII |  | 40.00 | 65.0 | −17.3 |
| XVIII |  | 40.00 | 65.0 | −13.9 |
| XIX |  | 25.00 | 95.0 | ... |
| XX |  | 40.00 | 95.0 | ... |

[a] See footnote *a*, Table III.

When ($\Delta^4$-cycloheptenyl)methyl and cycloheptylmethyl nitrosylate were compared, we found that the solvolysis of the unsaturated species, which has been claimed to be facilitated by $\pi$ participation,[10] is accelerated more than the saturated analog. Similarly, when one compares 2-cyclopentylethyl, 2-($\Delta^2$-cyclopentenyl)ethyl, and 2-($\Delta^3$-cyclopentenyl)ethyl nitrosylate, the latter has the most negative value for the activation volume. This agrees with other information suggesting $\pi$ participation in the solvolysis of the latter.[7,26] In the case of 2-($\Delta^3$-cyclohexenyl)ethyl nitrosylate there appears to be no $\pi$ participation; no cyclic products are formed and the rate is not significantly faster than that of the 2-cyclohexylethyl ester.[19c] (There probably is $\pi$ participation in formolysis.[27]) The pressure effects were the same within the limits of experimental uncertainty. In the case of cholesteryl and cholestanyl nitrosylate,[28] we were unable to get sufficiently accurate rates under pressure to draw any conclusions.

Thus, there appears to be a correspondence between the pressure effect on the rate constants of these solvolyses and the concepts of $\sigma$ and $\pi$ participation; hence, it is desirable to examine the weaknesses to which this correlation may be subject. The first question that might be raised is the validity of the $q^2$ dependence itself. Recent authors on the subject generally seem to have made use of this relation;[29] however, this assumption has one somewhat illogical consequence in that it implies equally efficient packing of dipolar solvent molecules regardless of which end of the dipole is pointed in the direction of the ion. There is, on the other hand, considerable evidence suggesting that the $q^2$ dependence must be substantially correct. Thus, it predicts that if the volume decrease for the first ionization step of a dibasic acid equal $\Delta V_{\text{I}}$, that for the second step should equal $2\Delta V_{\text{I}}$. One finds, in fact, for phosphoric acid, −16 and −26 cm$^3$/mole; for succinic acid, −10 and −13 cm$^3$/mole; for citric acid, −7, −10, and −16 cm$^3$/mole.[30] Thus, the effect is easily observable, though somewhat smaller than would be expected on the simple grounds just described (this must in part be due to the fact that the additional charges in the polyvalent ions do not reside in the same atoms). A similar effect is observed when ions are considered that have the same charge but differ in the degree of concentration of that charge. Thus, while for the large majority of carboxylic acids $\Delta V = -12 \pm 3$ cm$^3$/mole, for water $\Delta V = -22$ cm$^3$/mole; for phenol and *p*-nitrophenol $\Delta V = -17$ and $-10$ cm$^3$/mole, respectively, etc. There is unfortunately much less information available for bases, neither is there as wide a variety. Hence not too much can be quoted for the effect of delocalization on the electrostriction of cations (for ethylenediamine $\Delta V_{\text{II}}$ is 6 cm$^3$/mole larger than $\Delta V_{\text{I}}$, and for guanidine, $\Delta V$ is about 6 cm$^3$/mole larger than for ammonia[31]). It should be pointed out that the present study is by no means the first example of the use of charge dispersal as a factor in the interpretation of activation volumes. Brower, *et al.*,[32] attributed the change in magnitude of the positive activation volume in the decarboxylation of trihaloacetate anion (F > Cl > Br) to charge dispersal into empty d orbitals. Elsewhere, Brower[33] observed a pressure-induced shift in the equilibrium constant for the hydrolysis of $PtCl_4^{2-}$ to $PtCl_3(H_2O)^-$ in the direction of the former, and attributed this to charge concentration. Gonikberg, *et al.*,[34] invoked this factor to account for the solvent dependence of the activation volume of the exchange of radioiodide with *n*-propyl iodide, and Hamann used

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(25) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957).

(26) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

(27) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

(28) S. Winstein and R. Adams, *ibid.*, 70, 838 (1948); C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 3261 (1961).

(29) (a) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957); (b) S. D. Hamann, work cited in ref 23; (c) P. Mukerjee, *J. Phys. Chem.*, **65**, 740, 744 (1961); (d) S. W. Benson and C. S. Copeland, *ibid.*, **67**, 1194 (1963). However, Laidler has proposed a linear dependence: A. M. Couture and K. J. Laidler, *Can. J. Chem.*, **34**, 1209 (1956). Whalley has proposed a dissection of the solvation effect into polar, dipolar, and quadrupolar terms; however, it is too early to judge how useful this point of view will be in problems of the type studied here [E. Whalley, *J. Chem. Phys.*, **38**, 1400 (1963)].

(30) For recent compilations, see ref 29b and L. G. Hepler, *J. Phys. Chem.*, **69**, 965 (1965).

(31) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964).

(32) K. R. Brower, B. Gay, and T. L. Konkol, *J. Am. Chem. Soc.*, **88**, 1681 (1966).

(33) H. E. Brower, L. Hathaway, and K. R. Brower, *Inorg. Chem.*, **5**, 1899 (1966).

(34) (a) Y. A. Ershov, M. G. Gonikberg, M. B. Neiman, and A. A. Opekunov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **128**, 759 (1959); (b) Y. A. Ershov, V. B. Miller, M. B. Neiman, and M. G. Gonikberg, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1951 (1960).

it to explain the observation that, although this reaction is decreased in rate in acetone under pressure, the reactions of iodide with *n*-propyl chloride and bromide are accelerated[35]

$$^{-1/2}\mathrm{I}\cdots\mathrm{C}\cdots\mathrm{I}^{-1/2}\ \mathit{vs.}\ ^{-\delta}\mathrm{I}\cdots\mathrm{C}\cdots\mathrm{Cl}^{-(1-\delta)}$$

where $1 > \delta > 0$. Finally, Whalley[31] has applied this phenomenon to predict that N-protonated amides will be favored over their O-protonated isomers at high pressure. It seems therefore safe to conclude that charge dispersal will diminish the volume decrease, and the next question is, by how much?

It will be noted from the data in Tables III and IV that on the average the activation volume for the hydrolysis of benzenesulfonate esters in aqueous acetone is $-15$ to $-20$ cm$^3$/mole. If *ca.* one-half of this is due to the anion and if delocalization to a symmetrical species reduces the remainder to one-half (both of these conditions are consequences of the Drude–Nernst expression), then $\Delta V^*$ for the delocalized transition state should be about three-fourths of $\Delta V^*$ for the reaction progressing without $\sigma$ participation. The difference will be even smaller if in the transition state the ions are not yet fully formed, so that we may look to 4 or 5 cm$^3$/mole as an upper limit. Since for such reactions the solvent,[36] the temperature,[37] and the leaving group[21] may all affect the magnitude of $\Delta V^*$, it is important to limit comparisons to reactions occurring under otherwise identical conditions, and even then to esters of very similar structure. The data in Table III suggest that the activation volumes for the unassisted secondary esters are remarkably independent of the carbon skeleton, but those in Table IV show that the activation volumes for the unassisted primary esters exhibit some unexplained variations. Perhaps these find their origin in the greater conformational freedom. At any rate, in those cases where $\pi$ participation is involved, no prior estimate can be made; however, the one other example[23] of the use of $\pi$ participation as a factor in the interpretation of a large, negative activation volume may be useful for comparison.

A further question that must be asked is whether any other effects might complicate the interpretation. One known difference between *exo*- and *endo*-2-norbornyl esters is that the former are subject to internal return to some extent and the latter are not, the evidence being that resolved *exo* esters racemize during solvolysis at a rate faster than that of solvolysis.[38] As the molecule progresses from the initial state to completely separated ions, the volume will continuously diminish; in other words, the volume does not reach a minimum in the transition state. If one considers that it is more appropriate to use the polarimetric rate constant to express the ionization rate, another transition state is involved which is reached earlier and therefore will exhibit less electrostriction. In other words, one may confidently predict that the difference in activation volume between the *exo*- and *endo*-2-norbornyl brosylate solvolyses will be even greater than reported here if the reaction had been followed polarimetrically; this remains to be verified, however. Another effect that has been suggested for this reaction is steric hindrance to ionization;[19b] the present results found for the model compounds (cyclopentyl and cyclohexyl esters) resemble that of the *endo* ester, but not that of the *exo* epimer. The torsional effect recently proposed by Schleyer[39] cannot account for the results described here either.

The last, and, in our view, the only really serious question is concerned with the magnitude of the effect *vs.* the uncertainty of the measurements. It is a common phenomenon, and the data presented here bear this out, that the activation volume is not independent of the pressure; as a rule its absolute value declines as higher pressures are considered. This is related to the fact that highly dense transition states will generally be less compressible than the initial states and *vice versa.* In view of that fact, and since most chemists are primarily interested in data that apply under ordinary laboratory conditions, it has become common practice to use $\Delta V_0^*$, the activation volume at zero external pressure, as a basis for comparison. This now introduces a difficulty because the theoretical relation between the rate constant and the pressure is not known, and since the activation volume is related to the derivative of this expression, it will be clear that its magnitude depends somewhat on the method used to evaluate the slope of the plot $\ln k$ *vs.* $p$.[40] We have used the relation $\ln k = ap^2 + bp + c$; a recent study by Hyne[36] seems to have confirmed that that expression fits high-pressure rate data better than a number of alternatives. Actually, although the activation volumes change somewhat in value if other means of appraisal of the slope are employed, the differences between them, which are our principal concern here, are not very sensitive to this choice. Nevertheless, this is not an altogether satisfying state of affairs, and we have therefore begun to project our work in the direction of more precise evaluation of the rate constants at smaller time and pressure intervals by means of conductance measurements of solutions while these are under pressure. At the moment, our conclusion is that the results so far obtained are consistent with the concept of participation, but that further work is required to substantiate this agreement.

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(35) S. D. Hamann in "High Pressure Physics and Chemistry," Vol. II, R. S. Bradley, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 8.

(36) J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Am. Chem. Soc.*, **88**, 2104 (1966).

(37) Many examples of this can be found in ref 17.

(38) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).

(39) P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

(40) For reactions in nonpolar media involving no ions or charge separation an approximate relation between the pressure and the rate constant can be derived from the assumption that the transition state obeys the Tait equation [S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962)].